REPORT DOCUMENTATION PAGE

Form Approved OMB No. 0704-0188

1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE	3. REPORT TYPE AND DATES COVERED
	August 1992	Final Report, 1 Aug 91 - 31 Jul 92

4. TITLE AND SUBTITLE

Photoelectron and Chemielectron Spectroscopy of Metal Oxides of Atmospheric Importance

5. FUNDING NUMBERS

F6170891W0807

6. AUTHOR(S)

Prof J.M.Dyke

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

Department of Chemistry
University of Southampton
Southampton SO9 5NH, England

8. PERFORMING ORGANIZATION REPORT NUMBER

SPC-91-4004

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)

EOARD
PSC 802 BOX 14
FPO AE 09499-0200

10. SPONSORING/MONITORING AGENCY REPORT NUMBER

SPC-91-4004

11. SUPPLEMENTARY NOTES

12a. DISTRIBUTION/AVAILABILITY STATEMENT

Approved for public release; Distribution unlimited.

12b. DISTRIBUTION CODE

DISTRIBUTION STATEMENT A
Approved for public release
Distribution Unlimited

13. ABSTRACT (Maximum 200 words)

The contractor has characterized some chemionization reactions of Group II metals with atmospheric oxidants using electron spectroscopy and mass spectrometry. The contractor has measured the valence ionization energies of LiO, NaO and KO produced from the reactions of appropriate Group I metals with N_2O and O_3.

14. SUBJECT TERMS	15. NUMBER OF PAGES
	68
	16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19, SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
UNCLASSIFIED	UNCLASSIFIED	UNCLASSIFIED	UL

Final Report

on

Contract No. F6170891W0807

Contract Period 1.8.91.-31.7.92.

Principal Investigator: Prof. J.M. Dyke
Dept. of Chemistry
The University
Southampton SO9 5NH
U.K.

Title: *Photoelectron and Chemielectron Spectroscopy of Metal Oxides of Atmospheric Importance*

Products of the gas-phase reactions M + N_2O and M + O_3, where M=Na or K, have been investigated with u.v. photoelectron spectroscopy and the observed bands have been assigned with the assistance of results from *ab initio* molecular orbital calculations.

For the M + N_2O reactions, the observed products were MO + N_2. Measurement of the photoelectron bands associated with the metal monoxide, MO, allowed determination of the first adiabatic ionization energies (AIEs) of NaO and KO. The values obtained were AIE [$NaO(X^2\Pi)$] = (7.1 ± 0.1) eV and AIE [$KO(X^2\Pi)$] = (6.9 ± 0.1) eV. A similar study of the Li + N_2O reaction gave AIE [$LiO(X^2\Pi)$] = (7.6 ± 0.2) eV.

The reactions M + O_3 with M = Na or K, were observed to give MO + O_2 as the major reaction products. However, for each reaction a band was observed which was assigned to the first ionization energy of the secondary reaction product, MO_2. From the spectra obtained, the first adiabatic ionization energies of NaO_2 and KO_2 were measured as

AIE [$NaO_2(X^2A_2)$] = (6.2 ± 0.2) eV and

AIE [$KO_2(X^2A_2)$] = (5.7 ± 0.1) eV.

For both the M + N_2O and M + O_3 reactions, production of MO $A^2\Sigma^+$ was found to be favoured relative to production of the MO $X^2\Pi$ state, a result which has important implications in understanding the sodium night-glow in the mesosphere.

The ionization energy values determined in this work allow determination of ground state ionic dissociation energies. For example, for NaO^+ and KO^+ in their ground states, D_o has been derived as (0.60 ± 0.31) and (0.15 ± 0.14) eV respectively.

Reaction enthalpies can also be derived from the thermodynamic values derived in this work, for ion-molecule reactions of the type

$$MO + O_2^+ \rightarrow MO^+ + O_2 \qquad \ldots\ldots\ldots\ldots \qquad (1)$$

$$M^+ + O_3 \rightarrow MO^+ + O_2 \qquad \ldots\ldots\ldots\ldots \qquad (2)$$

For example for M = Na, ΔH_1 and ΔH_2 can be derived as -(4.98 ± 0.11) and (0.23 ± 0.44) eV respectively.

Work performed under this part of the contract, involving the study of Group I metals with oxidants, has been written up for publication and will soon be submitted to Journal of Chemical Physics. A preprint of this work is enclosed.

As part of an on-going experimental programme in chemiionization using chemielectron and chemiion spectroscopy, the ionization chamber of an electron spectrometer has been modified to allow ions and electrons to be sampled from the <u>same</u> reaction cell under a given set of experimental conditions simply by choosing the sign and magnitude of the extraction voltage on the cell. This experimental arrangement has been used to study the reaction of the group II metals (calcium, strontium and barium) with the oxidants $O_2(X^3\Sigma_g^-)$, $O_2(a^1\Delta_g)$ and $O(^3P)$. The results have been interpreted in terms of a simple thermodynamic model that is consistent with these reactions proceeding via long lived collision intermediates. The electron energy distributions have been interpreted in terms of a simple potential energy model, and the possibility

of the inclusion of an associative ionization reaction into a kinetic model of metal chemistry in the upper atmosphere has been considered. This work will soon be written up for publication.

Taking the Ba + $O_2(X^3\Sigma_g^-)$, Ba + $O_2(a^1\Delta_g)$ and Ba + $O(^3P)$ reactions as examples, the electron energy distributions and ions seen in the Ba + $O_2(X^3\Sigma_g^-)$ case can be interpreted in terms of the following processes:

$$Ba + O_2(X^3\Sigma_g^-) \rightarrow BaO_2^* \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (3)$$

$$BaO_2^* + Ba \rightarrow Ba_2O_2^+ + e^- \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (4)$$

Adding $O_2(a^1\Delta_g)$ to the Ba + $O_2(X^3\Sigma_g^-)$ reaction mixture reduces the ion and electron yield by removing Ba atoms via the neutral reaction

$$Ba + O_2(a^1\Delta_g) \rightarrow BaO^* + O \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (4)$$

Chemiionization can, however, occur via

$$BaO^* + Ba \rightarrow Ba_2O^+ + e^- \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (5)$$

On adding $O(^3P)$ to the system, BaO is produced via

$$Ba + O(^3P) \rightarrow BaO^* \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (6)$$

which then undergoes chemiionization via reaction (5)

The new apparatus proved very useful in distinguishing between primary and secondary ions via the saturation current method, and in associating a given primary ion to an observed chemielectron band. The high kinetic energy offsets of the experimental chemielectron bands were used to estimate the exothermicities of the observed chemiionization reactions. Negative ion formation, a competing process to electron production in chemiionization, has also been investigated for the Group II metal plus oxidant reactions and in each case negative ion production has been found to be a minor channel.

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Form Approved
OMB No. 0704-0188

1. AGENCY USE ONLY (*Leave blank*)

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PHOTOELECTRON AND CHEMIELECTRON SPECTROSCOPY OF METAL OXIDES OF ATMOSPHERIC IMPORTANCE

5. FUNDING NUMBERS
F6170891W0807

6. AUTHOR(S)
PROFESSOR J.M. DYKE

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
University of Southampton
Department of Chemistry
Highfield
Southampton SO9 5NH, UK

8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)
Sponsoring/Monitoring Agency: European Office of Aerospace Research and Development, PSC 802 Box 14, FPO AE 09499-0200

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The contractor has measured the valence ionization energies of LiO, NaO and KO produced from the reactions of appropriate Group I metals with N_2O and O_3.

The results of both investigations are documented in a final report which has been delivered at the end of the contract.

14. SUBJECT TERMS
Chemielectron Spectroscopy   Ionic Heats of Formation
Photoelectron Spectroscopy   Charge Exchange Reactions
Ionization Energies   Chemiionization   Chemiion Mass Spectrometry

15. NUMBER OF PAGES

16. PRICE CODE

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UNCLASSIFIED	UNCLASSIFIED	UNCLASSIFIED	

REPORT OF INVENTIONS AND SUBCONTRACTS
(Pursuant to "Patent Rights" Contract Clause) (See Instructions on Reverse Side.)

Form Approved
OMB No. 0704-0240
Expire Sep 30, 1988

1a. NAME OF CONTRACTOR/SUBCONTRACTOR J.M. DYKE	c. CONTRACT NUMBER F6170891W0807	2a. NAME OF GOVERNMENT PRIME CONTRACTOR	c. CONTRACT NUMBER	3. TYPE OF REPORT (X one) a. INTERIM [X] b. FINAL
b. ADDRESS (Include ZIP Code) THE UNIVERSITY SOUTHAMPTON, SO9 5NH, UK	d. AWARD DATE (YYMMDD)	b. ADDRESS (Include ZIP Code)	d. AWARD DATE (YYMMDD)	4. REPORTING PERIOD (YYMMDD) a. FROM 91.08.01 b. TO 92.07.31

SECTION I - SUBJECT INVENTIONS

5. "SUBJECT INVENTIONS" REQUIRED TO BE REPORTED BY CONTRACTOR/SUBCONTRACTOR (If "None," so state)

a. NAME(S) OF INVENTOR(S) (Last, First, MI)	b. TITLE OF INVENTION(S)	c. DISCLOSURE NO., PATENT APPLICATION SERIAL NO. OR PATENT NO.	d. ELECTION TO FILE PATENT APPLICATIONS (1) United States (a) Yes	(1) United States (b) No	(2) Foreign (a) Yes	(2) Foreign (b) No	e. CONFIRMATORY INSTRUMENT OR ASSIGNMENT FORWARDED TO CONTRACTING OFFICER (1) Yes	(2) No
NONE	NONE							

f. EMPLOYER OF INVENTOR(S) NOT EMPLOYED BY CONTRACTOR/SUBCONTRACTOR		g. ELECTED FOREIGN COUNTRIES IN WHICH A PATENT APPLICATION WILL BE FILED	
(1)(a) Name of Inventor (Last, First, MI)	(2)(a) Name of Inventor (Last, First, MI)	(1) Title of Invention	(2) Foreign Countries of Patent Application
(b) Name of Employer	(b) Name of Employer		
(c) Address of Employer (Include ZIP Code)	(c) Address of Employer (Include ZIP Code)		

SECTION II - SUBCONTRACTS (*Containing a "Patent Rights" clause*)

6. SUBCONTRACTS AWARDED BY CONTRACTOR/SUBCONTRACTOR (If "None," so state)

a. NAME OF SUBCONTRACTOR(S)	b. ADDRESS (Include ZIP Code)	c. SUBCONTRACT NO.(S)	d. DFAR "PATENT RIGHTS" (1) Clause Number	(2) Date (YYMM)	e. DESCRIPTION OF WORK TO BE PERFORMED UNDER SUBCONTRACT(S)	f. SUBCONTRACT DATES (YYMMDD) (1) Award	(2) Estimated Completion

SECTION III - CERTIFICATION

7. CERTIFICATION OF REPORT BY CONTRACTOR/SUBCONTRACTOR (Not required if [ ] Small Business or [ ] Non-Profit organization.) (X appropriate box)

a. NAME OF AUTHORIZED CONTRACTOR/SUBCONTRACTOR OFFICIAL (Last, First, MI) J.M. DYKE	c. I certify that the reporting party has procedures for prompt identification and timely disclosure of "Subject Inventions," that such procedures have been followed and that all "Subject Inventions" have been reported.	
b. TITLE PROFESSOR	d. SIGNATURE J M Dyke	e. DATE SIGNED 92.07.14

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